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(Statement A)

MODEL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE THIN FILMS FOR COATING APPLICATIONS

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ABSTRACT:

The possibility of forming Polyhedral Oligomeric Silsesquioxanes (POSS) based coatings is considered. Surfactant POSS molecules (containing hydrophilic silanol "head" groups and hydrophobic organic coronas) are spread on water in a Langmuir Blodgett apparatus and the surface pressure-area relationships are determined and correlated to the structure of the POSS surfactant. Langmuir-Blodgett transfer of surfactant POSS onto silicon substrates is considered as a model "dip coat" application; however, POSS monolayers do not appear to be sufficiently stable to undergo Langmuir Blodgett transfer. The thin film stability is discussed.

KEYWORDS: POSS, monolayer, Langmuir-Blodgett.

1. INTRODUCTION:

Polyhedral Oligomeric Silsesquioxanes (POSS) have been developed at the Air Force Research Laboratory for advanced defense applications. POSS is an organic-inorganic hybrid nanoparticle consisting of a silica-like core surrounded by an organic R group corona. (Figure 1). These materials are used to form polymeric nanocomposites that have enhanced thermomechanical properties, atomic oxygen and space resistance, oxidation resistance, etc. Specific applications and physical properties are discussed elsewhere in this volume. However, many potential desirable properties of a nanocomposite hybrid material (enhanced scratch, ablation, corrosion, and fire resistance) might be obtained if the POSS was applied as a thin coating. In a similar vein, traditional composites or adhesives could have the interfaces modified by POSS coatings. It is expected that any improved properties would be especially sensitive to film defects which could act as a loci for failure and undercutting of the residual film. It is thus crucially important that uniform stable films be developed.
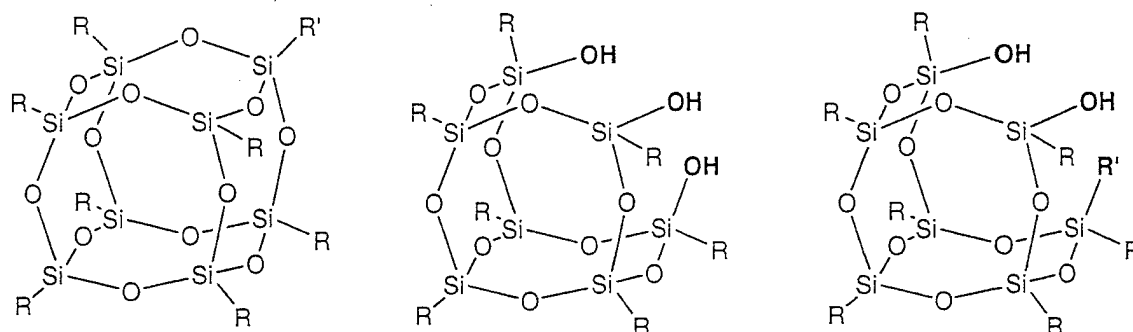
Figure 1 POSS structures used in this study-fully condensed cube (left), incompletely condensed trisilanol (middle) and a modified diisilanol (right)

POSS materials are formed by the controlled hydrolysis and condensation of various trichloro and/or trialkoxysilanes. An interesting synthetic variant is the formation of incompletely condensed POSS siloxanes. The most common incompletely condensed POSS is shown in Figure 1(middle). The three silanol groups should be hydrophilic and thus act as an anchor on the water surface. The presence of hydrophilic and hydrophobic regions suggest that incompletely condensed POSS would be reasonably surface active.[1]

The Langmuir Blodgett technique has been used to characterize surface active materials (surfactants) at the air water interface.[2] Langmuir Blodgett transfer of single molecular layers (monolayers) is often possible by a controlled "dip coat" method, and repeated dipping cycles *could* produce uniform coatings of precisely controlled thickness and film structure. This report details the efforts at characterizing the single component POSS thin films at the air water interface. These results should serve as benchmarks for understanding the structure property relationships that occur in POSS based thin films.

2. EXPERIMENTAL:

All POSS "cubes" of nominal 95+% purity were obtained from Hybrid Plastics (Fountain Valley, CA). Hybrid Plastics' shorthand acronyms for POSS will be used for simplicity-in Figure 1a, POSS with R=R'=Cp=cyclopentyl and chemical formula $Si_8O_{12}(C_5H_9)_8$ would be abbreviated as Octacyclopentyl POSS. Similarly, an incompletely condensed POSS with ethyl substituents in Figure 1b with molecular formula $Si_7O_9(CH_3CH_2)_7(OH)_3$ would be known as ethyl trisilanol POSS. The following materials were used in this study: octacyclopentyl ($Si_8O_{12}(C_5H_9)_8$ MW=969.60 g/mol), ethyl trisilanol ($Si_7O_9(C_2H_5)_7(OH)_3$ MW=595.04 g/mol); cyclopentyl trisilanol ($Si_7O_9(C_5H_9)_7(OH)_3$ MW=875.50 g/mol) isobutyl trisilanol ($Si_7O_9(C_2H_9)_7(OH)_3$ MW= 791.42 g/mol) fluoro(13)cyclopentyldisilanol ($Si_7O_9(C_5H_9)_7(OH)_2(OSi(CH_3)_2(CF_2)_5CF_3)$ MW=1279.75 g/mol).

Solutions of 0.5-2 mg/ml POSS in chloroform were prepared. A NIMA mini LB trough was used for the Langmuir Blodgett experiments. A paper Wilhelmy plate was used to

measure surface pressure in the normal manner. The Teflon surfaces of the trough and barriers were cleaned with HPLC grade isopropanol and chloroform, and then filled with deionized water (18.2 MΩ, 4ppb organics, Gradient A10 System, Millipore Corp) to a level approximately 4 mm above the bottom of the movable barrier. The water surface was cleaned via micropipette "vacuuming" and thermostatted to 25 °C. 50 μL of the POSS solutions were spread on the water subphase and the chloroform was allowed to evaporate, leaving pure POSS on the water surface. The barriers were compressed at 10 cm/min to generate the relevant surface pressure-area relationships.

3. RESULTS AND DISCUSSION

3.1 Langmuir Blodgett Isotherms:

The Langmuir-Blodgett technique can be envisioned as a two dimensional analog of the compression of a gas. Surfactant materials that are well dispersed (e.g. at large surface areas) are "gas like" with small intermolecular interactions and resultant low surface pressures. As the material is compressed, the surface pressure will increase as the molecules become forced into contact. The condition where the molecules are in uniform close contact (the monolayer) is reflected by a local rapid increase in the surface pressure. An extrapolation of this increase to zero surface pressure would thus be indicative of the excluded area of the surfactant. Increasing compression results in progressive structural changes. In analogy to the gas compression model, a horizontal "tie line" would represent liquid-gas coexistence and progressive conversion to a more condensed state. A characteristic transition from increasing surface pressure to the coexistence regime is known as "monolayer collapse." Continued compression should effectively change the pseudo 2-D liquid state into a true "bulk" phase that is effectively incompressible (rapidly increasing surface pressure in a very small compression area regime).
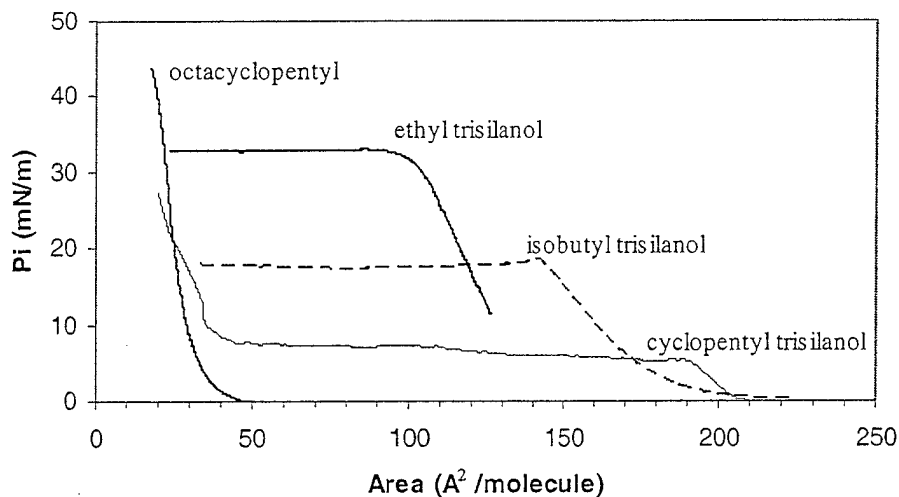

Figure 2 Langmuir Blodgett Surface Pressure Area Relations for Surfactant POSS

The surface pressure-area isotherm at 25°C of various POSS is presented in Figure 2. The fully condensed octacyclopentyl POSS shows a single vertically asymptotic increase in surface pressure at approximately 33 Å^2. A POSS molecule with diameter of 12 Å (equivalent to the longest distance between vicinal carbons bonded to opposed silicons on a POSS cage) would have a cross sectional area of 150 Å^2. The extrapolated area of the octamethyl POSS is seen to be far too small for any characteristic dimension of the POSS cage, and thus indicates that this molecule does not exist as a monolayer on the surface, but instead as 3 dimensional aggregates that become an incompressible bulk phase. It can be easily shown that fully condensed POSS have effectively the same Langmuir Blodgett asymptote at very small surface areas (ca. 30-50 Å^2). Thus, uniformly hydrophobic POSS is not thought to be a surfactant, and would not be suitable for Langmuir Blodgett film transfer.

Cyclopentyl, Cyclohexyl, and Ethyl trisilanol POSS all show an increase in surface pressure at large surface area. This is clear indication that these POSS silanols form monolayers on a water surface. The extrapolated area at 0 surface pressure varies as a function of the size of the hydrophobic R group substituent, ranging from 140 Å^2 for ethyl, to 185 Å^2 for isobutyl, to 205 Å^2 for cyclopentyl substituents. These extrapolated areas are not as large as would be expected if the R groups were fully extended from the silica-like core and had no intermolecular interpenetration (area in excess of 220 Å^2), nor completely folded against the cube face (having an extrapolated area of approximately 150 Å^2), This indicates that the R groups have some conformational freedom-either via free volume "holes" that favor interpenetration, or via R group flexibility. This finding is in accord with the Chem3D(CambridgeSoft) generated molecular model of cyclohexyl trisilanol based on single crystal X-ray coordinates with appropriate van Der Waals radii. This model indicates that the cyclohexyl R groups have no apparent specific orientation. The hydrophobic covering does not completely occlude the POSS core, and there appears to room to accommodate intermolecular interpenetration. Furthermore, the hydrophilic headgroup "pocket" is apparent (shown at the bottom of the figure), and the hydrophobic groups do no appear to significantly impact into the headgroup plane.

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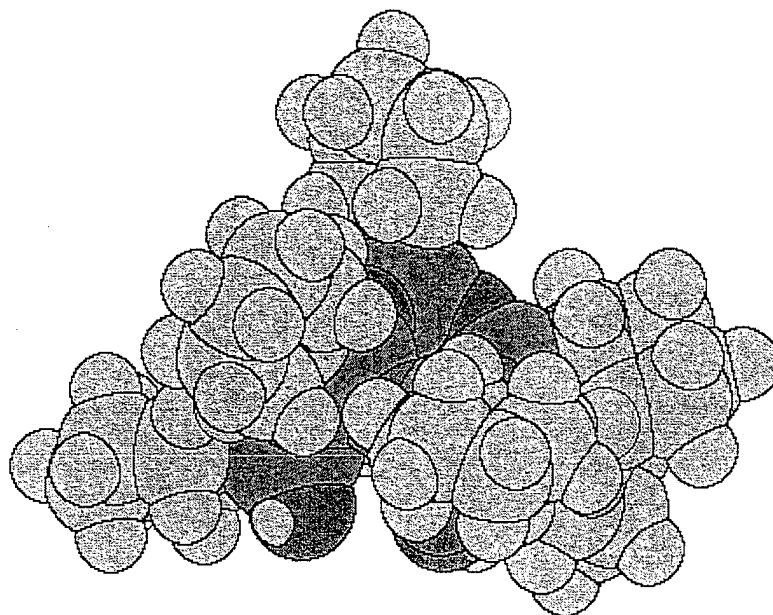
Figure 3 Xray crystal stucture of cyclohexyltrisilanol POSS.

The plateau pressures (collapse pressure) vary strongly for the different R groups. The large cyclopentyl trisilanol has the lowest collapse/plateau pressure, ca 6 mN/m, with isobutyl trisilanol having a collapse pressure of 18 mN/m, and ethyl trisilanol having a collapse pressure of 32 mN/m. A detailed description of the collapse pressures (and concomitant shape of the surface pressure-area diagram) is beyond the scope of this work. However, the collapse pressure is the key design factor for attempting Langmuir-Blodgett transfer (vide infra) and it may be expected that different POSS would have different thin film stability.

Finally, the cyclopentyl triol is noted to have a secondary transition to the asymptotically increasing incompressible regime. The onset of this transition is very similar to the uniformly hydrophobic octacyclopentyl materials. A collapse event whereby the hydrophilic "pockets" for differing POSS trisilanols pair may be imagined. This dimer would have a uniform hydrophobic coating. As is the case for the octacyclopentyl POSS, the high surface pressure condensed phase would probably not be suitable for Langmuir Blodgett transfer.

3.2 Modified POSS Surfactants:

POSS trisilanols are often used as scaffolds for functionalization. Most often, this is achieved by "corner capping" with a suitable trichlorosilane (R'SiCl₃) to reform the completely condensed POSS cube having one corner with a differing (most often reactive) R' group.(Figure 1a).However, it has been noted by Ducheteau that the silanols in a POSS trisilanol have different acidity, likely due to cooperative hydrogen bonding effects/[DucPateau]. [3]By extension, it can be assumed a given silanol would have much

[handwritten annotations in margins: "period should go after C)", "(delete)", ""effects.³""]

higher reactivity, and as a result a POSS trisilanol can effectively be converted into a functionalized POSS disilanol (Figure 1c). In this case, a cyclopentyl POSS trisilanol is condensed with a (1-ethyltridecafluorohexyl)dimethyl chlorosilane to form fluro(13)cyclopentyl disilanol (Figure 4). This synthetic variant should emulate a traditional surfactant having a long chain hydrophobe with a hydrophilic silanol "headgroup."
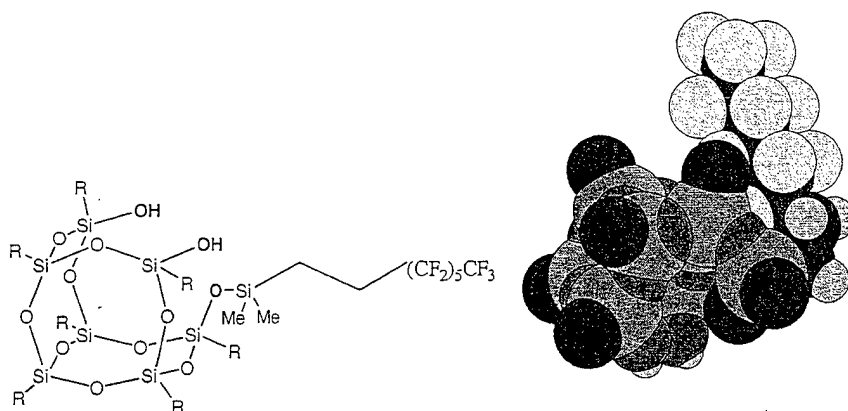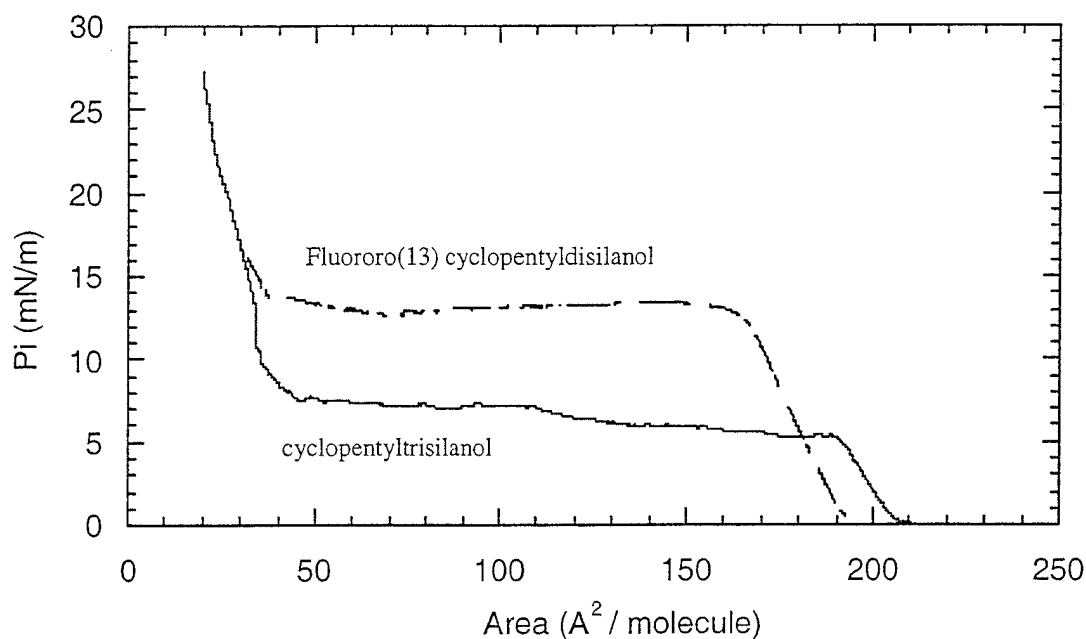

Figure 4 Modified POSS Surfactants. A long chain flouroalkyl group makes the POSS disilanol more closely resembly standard surfactants. The Langmuir Blodgett isotherm (top) indicates monolayer formation.

Prima facie, geometrical arguments suggest that the tridecafluoro cyclopentyl disilanol should not be an effective surfactant. The rigid hydrophobic fluroalkyl segment is oriented toward the hydrophilic head group, and would appear to be forced into the water subphase. The low surface energy of fluorinated moieties should dictate that the fluoroalkyl surface segregate and orient away from the water layer. However, in Figure 3, it is obvious that tridecafluoro cyclopentyl disilanol POSS is a surfactant with a surface pressure-area relationship very similar to the precursor cyclopentyl trisilanol. The surface pressure rise, plateau, and low area asymptote occur at the approximately the same areas (although it is unknown if the difference in plateau pressure is significant.) This behavior can be rationalized by considering a molecular model of the modified surfactant (Figure 4 bottom right). This model was generated with Chem3D based on the X-ray crystal structure of a disilanol homolog (trimethyl cyclopentyl disilanol, $Si_7O_9(C_5H_9)_7(OH)_2(OSi(CH_3)_3$ MW=947.69 g/mol) One methyl group was replaced with an ethyltridecafluorohexyl group-the orientation was arbitrarily chosen to avoid the subphase, however, the energy minimization protocol found this to be a reasonable structure. The POSS cage and siloxane spacer group impart enough flexibility so that both the fluoroalkyl hydrophobe and the cyclopentyl corona are completely excluded from the interface (for clarity, only the bonded carbon in of the cyclopentyl groups was shown). Furthermore, the reduction in the hydrophilic character does not preclude the POSS disilanol from forming a monolayer.

3.3 Langmuir Blodgett Transfer Experiments

Langmuir Blodgett transfer onto a surface is conducted by generating a dense monolayer (i.e. compression from high areas, low surface pressures to a surface pressure close to, but before the collapse plateau.) A substrate is dipped through the monolayer, and compression is continued to maintain a constant surface pressure. In general, POSS surfactants do not maintain a given precollapse surface pressure, but instead slowly decay, indicating rearrangement of the surfactant structure in a manner analogous to collapse. As might be expected, the trial film that was deposited onto a cleaned silicon (100) wafer substrate was irregular and flawed when Langmuir Blodgett transfer was attempted. The choice of substrate and preparation of the surface will have a large effect on the Langmuir Blodgett transfer efficiency, and will be the subject of further investigation. For example, a hydrophilic surface will tend to favor bonding to the hydrophilic groups, which could occur on an upstroke (raising the substrate through the water subphase) whereas a hydrophobic (silane treated) surface would tend to favor close contact with the hydrophobe and concomitant expression of the hydrophilic head group at the air-monolayer interface. Similar effects will occur on repeated dippings to form multilayer structures, and will also be the focus of continued research.

For purposes of comparison, chlorosilane self assembled monolayers (SAM-Figure 5) are known to effectively Langmuir Blodgett transfer over a wide range of surface pressures (20-50 mN/m). Chlorosilane SAM monolayers are of interest because of their inherent resilience and thin film toughness[4] (esp. when compared to other similar Langmuir Blodgett films-long chain alkyl carboxylic acids, etc.) For the purposes of this discussion, we only consider the case where a hydrophilic silicon substrate is raised from

the water layer to the air layer. This mechanism should give a monolayer where the hydrophilic silanols are tethered to the silicon surface.
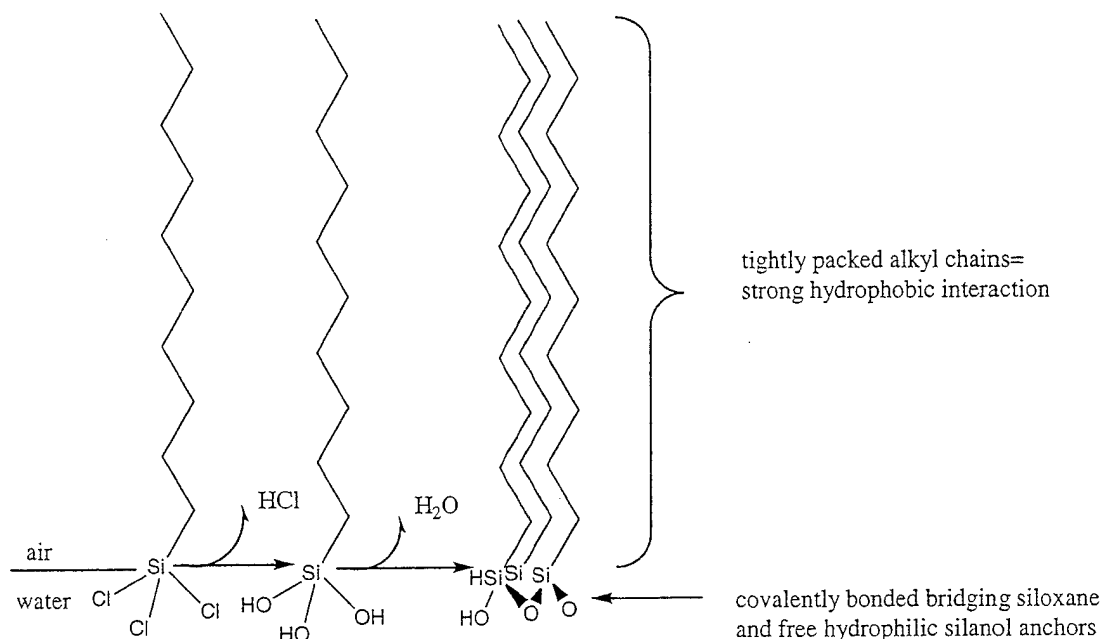

tightly packed alkyl chains= strong hydrophobic interaction

air

water

HCl   H₂O

covalently bonded bridging siloxane and free hydrophilic silanol anchors

Figure 5 Formation of Chlorosilane Self Assembled Monolayers

Chlorosilane SAMs are formed by spreading a long chain trichlorosilane onto a water surface. The water subphase hydrolyzes the silicon-chlorine bonds to form silanols, which are reactive with other silanols and spontaneously condense. The self assembly of chlorosilane SAMs is thought to arise from a combination of the packing of the hydrophobic tails and the bridging/condensation of the formed silanols at the surface. This in turn provides for an unusually stable monolayer film. The bridging interactions are not complete, and a few free silanols remain which are apparently sufficient to anchor to both the water subphase and the transfer substrate. Longer chain hydrophobic groups can tightly pack into a crystal-like matrix. The failure of POSS to Langmuir Blodgett transfer is likely due to failure in both of these modes. The hydrophobic corona which surrounds the POSS trisilanol pocket prevent[6] the silanols from forming stable intermolecular siloxane bridges. Indeed, it is this hydrophobic covering that can allow stable trisilanols to be isolated. Hydrophobic interactions among the corona R groups also are not sufficient to stabilize the monolayer film for transfer. The long fluoroalkyl chain (Figure 4)is probably not long enough to have significant fluroalkyl-fluoroalkyl packing. POSS modified surfactants with longer alkane chains, or different corona functionality, might have sufficient conformational freedom for stronger hydrophobic interactions. Cadmium salts are often dissolved into the water subphase to bridge between the headgroups in fatty acid surfactants and allow for Langmuir Blodgett transfer, and a similar approach may work for POSS surfactants. These approaches, and use of co-transfer agents (likely polymeric) will be key for forming controlled thin films.

4. CONCLUSIONS:

A variety of surfactant POSS molecules have been identified. The Langmuir-Blodgett isotherms of single component POSS thin films have been established at the air-water interface. POSS molecules containing free silanols form monolayers, whereas POSS having a hydrophobic corona (from complete condensation of the POSS or via dimer formation) appear to form incompressible aggregates. The extrapolated excluded volume area varies for different POSS corona R groups (smaller R groups give a material with smaller excluded area.) The absolute magnitude of the extrapolated excluded area suggest that there is some conformational freedom vis a vis the orientation and spacing of the R groups. The surface pressure (in particular the collapse plateau) also varies with the POSS R group size, with smaller R groups having larger collapse pressures. These monolayers likely can not be effectively transferred to a substrate in the traditional manner. This failure indicates that mechanisms that stabilize chlorosilanes SAMs for transfer do not apply to POSS, and different transfer paradigms are needed.

'cannot' is one word

5. ACKNOWLEDGMENTS

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author name should not be underlined